Lifetimes of Some Styrene Triplets in Fluid Solution. Triplet Geometries and the Effect of Alkylation

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Olefin triplets occupy a central position in mechanistic organic photochemistry.[1] If twisted extensively, they may be described as "1,2 biradicals". Decay pathways and dynamic behavior of such biradicals and biradicaloids are topics of much current interest.[2] However, measurements of olefin triplet lifetimes and their structural dependences are only now becoming common.[3] Using the technique of electron-transfer quenching with paraquat dication (PQ^{2+}), we have examined the lifetimes of a series of styrene triplets in methanol at room temperature. We find that the relaxed geometry of styrene triplets is the twisted one, acyclic styrene triplets show much shorter lifetimes than those constrained to near planarity by a small ring, and alkylation at the double bond increases the triplet lifetime. Our results so far suggest that intersystem crossing of the twisted species is the lifetime-determining factor for acyclic styrene triplets, and that the rate for this depends at least in part on motions of the vinyl hydrogens.

Equations 1–4 describe the essential chemistry.[4] The (first-order) rise of the absorption of $PQ^{+}\cdot$ monitored at 395 or 600 nm after nitrogen laser excitation follows eq 5,[5] and k_{PQ} and τ are

$$Ph_2CO \xrightarrow{3377\ \text{Å}} \rightsquigarrow {}^3Ph_2CO \qquad (1)$$

$$^3Ph_2CO + \text{olefin} \rightarrow Ph_2CO + {}^3\text{olefin} \qquad (2)$$

$$^3\text{olefin} + PQ^{2+} \xrightarrow{k_{PQ}} {}^2\text{olefin}^{+}\cdot + {}^2PQ^{+}\cdot \qquad (3)$$

$$^3\text{olefin} \xrightarrow{\tau^{-1}} \text{olefin } (S_0) \qquad (4)$$

$$k_{\text{rise}} = \tau^{-1} + k_{PQ}[PQ^{2+}] \qquad (5)$$

obtained from least-squares plots. Previous studies of structures and the factors which influence the decay of olefin triplets in solution are largely limited to the stilbenes.[6] It is known[6] that, in fluid solution, the stilbene triplet is a rapidly equilibrating mixture of transoid (^{3}t) and twisted (^{3}p) geometries, with ^{3}p somewhat the more stable.[7] Long lifetimes are observed for a planar analogue[8] and acyclic stilbenes in rigid matrix.[9] In fluid solution, the sensitized cis–trans isomerization quantum yield is high,[10] and ^{3}p can be intercepted.[11] These results make it clear that the lifetime of 50[7]–100 ns[12] reported for stilbene triplets in solution is determined by the rate of T_1–S_0 intersystem crossing at the ^{3}p geometry and not the rate of the $^3t \rightarrow {}^3p$ process. A report[13] in the literature of a systematic study of phenylcycloalkene triplet lifetimes suggested that the decay rates for these styrene chromophores could be correlated with activation energies for twisting from the planar structure to the crossing for the T_1–S_0 potential-energy surfaces. The implication that the lifetimes reported related to the $^3t \rightarrow {}^3p$ rate, not the T_1–S_0 rate, would be a mechanistic contrast to the stilbene case if it were true for acyclic examples.

Table I. Lifetimes and k_{PQ} Values for Triplets

compd[a]	τ, ns[d]	k_{PQ}, 10^9 $M^{-1}\ s^{-1}$ [d]
$AnCH{=}CH_2$ (**1**)	22 ± 1	1.1 ± 0.6
$AnCH{=}CHCH_3$ (**2**)[b]	30 ± 2	4.8 ± 0.7
$AnCD{=}CDCH_3$ (**3**)[b]	34 ± 1.5	4.1 ± 0.5
$AnC(CH_3){=}CH_2$ (**4**)	31 ± 3.5	1.64 ± 0.37
$AnCH{=}CHCH_2Ph$ (**5**)[b,e]	34 ± 3	3.1 ± 0.4
$AnC(C_2H_5){=}CHCH_3$ (**6**)[c]	38 ± 4	0.35 ± 0.05
$AnCH{=}C(CH_3)_2$ (**7**)	48 ± 5	1.2 ± 0.34
$AnC(CH_3){=}C(CH_3)_2$ (**8**)	91 ± 9	1.4 ± 0.34
$PhCH{=}CHCH_3$ (**9**)[b]	46 ± 2	0.65 ± 0.04
anisylcyclopentene (**10**)	≳1 μs[f]	6 ± 1
phenylcyclopentene (**11**)	≳1 μs[f]	4.5 ± 1

[a] Compounds were synthesized by Grignard additions and subsequent dehydrations except for the commercially available **2** and **9**. Purity of synthesized compounds ranged from 97 to 99.5+%. [b] Trans reactant. [c] Approximately equal mixture of *E* and *Z* isomers. [d] Errors are taken as twice the standard deviations of the intercept (τ^{-1}) and slope (k_{PQ}) of least squares plots of eq 5 in text. [e] Prepared by Dr. K. Mizuno by hydrogenation of *p*-methoxychalcone, reduction to the carbinol ($NaBH_4$), and dehydration with TsCl in pyridine. [f] Lifetimes are too long to measure conveniently with present technique owing apparently to intervention of second-order decay processes, the pulse intensities being such that a second-order component to the decay requires microsecond or longer lifetimes. Values of k_{PQ} are obtained at concentrations of PQ^{2+} high enough (ca. 10^{-3}M) for good first-order plots to be obtained and are thus no more imprecise than the other values reported.

The lifetimes we have determined (see Table I) range from ca. 20–100 ns, not unexpected in light of early estimations[14] of spin–orbit coupling in related biradicals and biradicaloids. The effect of alkylation is most striking. The monosubstituted **1** (22 ns), disubstituted **2**–**5** (30–34 ns), trisubstituted **6** and **7** (38–48 ns), and tetrasubstituted **8** (91 ns) anisylalkenes clearly show the tendency for increasing alkylation at the double bond to increase the lifetime. Since increasing alkylation should increase the rate of twisting of planar triplets (by increasing the relief of strain upon twisting), the ordering of lifetimes noted rules out the $^3t \rightarrow {}^3p$ process as contributory to the lifetimes in the acyclic cases. We conclude that the $^3t \rightarrow {}^3p$ process is rapid and the lifetimes are determined by the rate of the $T_1 \rightarrow S_0$ process as for the stilbenes. Whether twisting contributes to the lifetimes of small-ring arylcycloalkenes such as **10** or **11** is, however, still moot. Their approximately microsecond lifetimes may well be determined by the barrier to twisting as previously suggested.[13]

We believe that ^{3}p is in fact the only significant species present for acyclic styrene triplets in fluid solution. The effect of azulene

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(1) See N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Menlo Park, CA, 1978, pp 473ff.

(2) See J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).

(3) Stilbenes: (a) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 446 (1974); (b) H. Gorner and D. Schulte-Frohlinde, *ibid.*, **82**, 2653 (1978); (c) see R. Bonneau, *J. Am. Chem. Soc.*, **102**, 3816 (1980) for a study of enone triplets; (d) see A. J. G. Barwise, A. A. Gorman, and M. A. J. Rodgers, *Chem. Phys. Lett.*, **38**, 313 (1976) for triplet norbornene; (e) Bonneau [R. Bonneau, *J. Photochem.*, **10**, 439 (1979)] reports lifetimes for styrene triplets in the same general range that we observe. We also thank Dr. Bonneau for a private communication describing more recent work.

(4) Evidence for this scheme as the source of the transient observed has been presented previously: R. A. Caldwell and C. Pac, *Chem. Phys. Lett.*, **64**, 303 (1979). In general, the absence of any ketyl absorption upon quenching of $^3Ph_2CO$ by any of the olefins confirms the absence of an electron—or hydrogen atom—transfer occurring parallel to eq 2, and the high (0.08–0.25 M) concentration of olefin ensures that eq 2 dominates all other possible fates of $^3Ph_2CO$ under our conditions.

(5) Kinetics of the identical form are used to interpret the formation of $PQ^{+}\cdot$ from Norrish II biradical precursors: R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828, 2126 (1977); **82**, 2662 (1978).

(6) An excellent recent summary is J. Saltiel and J. L. Charlton, in "Rearrangements in Ground and Excited States", Vol. 3, P. deMayo, Ed., Academic Press, 1980, pp 25ff.

(7) H. Görner and D. Schulte-Frohlinde, private communication.

(8) J. Saltiel *et al.*, *Pure Appl. Chem.*, **41**, 559 (1975).

(9) J. Saltiel, G.-E. Khalil, and K. Schanze, *Chem. Phys. Lett.*, **70**, 233 (1980).

(10) (a) G. S. Hammond *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964); (b) H. A. Hammond, D. E. DeMeyer, and J. L. R. Williams, *ibid.*, **91**, 5180 (1969).

(11) (a) R. A. Caldwell and R. E. Schwerzel, *J. Am. Chem. Soc.*, **94**, 1035 (1972); (b) R. E. Schwerzel and R. A. Caldwell, *ibid.*, **95**, 1382 (1973); (c) J. Saltiel and B. Thomas, *ibid.*, **96**, 5660 (1974); (d) J. Saltiel and B. Thomas, *Chem. Phys. Lett.*, **37**, 147 (1976).

(12) F. S. Dainton, E. A. Robinson, and G. A. Salmon, *J. Phys. Chem.*, **76**, 3897 (1972).

(13) H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *J. Am. Chem. Soc.*, **97**, 3718 (1975).

(14) L. Salem and C. Rowland, *Angew. Chem.*, *Int. Ed. Engl.*, **11**, 92 (1972).

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on cis–trans photostationary ratios[10a] is diagnostic for the presence of ^{3}t. Our previous[11b] observation of the absence of an azulene effect for β-methylstyrene (**9**) required either a very short triplet lifetime or a negligible fraction of ^{3}t present. The lifetime we now report for triplet **9** would be quite sufficient to permit observation of an azulene effect if even 5% of the triplets are transoid, and the absence of the effect now requires that ^{3}p be the only species present in significant amount. This conclusion finds theoretical support.[3e]

The values for k_{PQ} we report nicely reinforce our conclusion of a twisted structure. If the triplets were planar, increasing alkyl substitution would increase k_{PQ}, since the olefin triplet would thereby be a better electron donor. Although k_{PQ} increases (see Table I) on going from *p*-methoxystyrene (**1**) to 1-(*p*-methoxyphenyl)propene (**2**), it decreases for the dimethyl and trimethyl analogues **7** and **8**, in contrast to the prediction for a series of planar triplets. That k_{PQ} attains a maximum for an intermediate degree of substitution can be rationalized easily for twisted triplets as resulting from a balance of two effects. The increased electron-donating ability of the olefin will tend to increase k_{PQ}, and the increased steric hindrance to reaching planarity will tend to decrease k_{PQ}, as the degree of alkylation increases. We believe that the planar geometry is the preferred one for electron transfer, both from the observed high values of k_{PQ} for the near-planar arylcyclopentenes and from the expectation of a planar geometry for the styrene radical cation produced.

The effect of alkyl substitution may relate fundamentally to the mechanism of T_1–S_0 intersystem crossing. We suggest that the effect of alkylation upon the lifetimes of the twisted triplets arises in substantial part from the contribution of vinyl C–H vibrational modes to triplet decay. Saltiel et al.[15] have reported a substantial effect of vinyl deuterium on the stilbene triplet lifetime. We find a value of 1.11 ± 0.07 (two standard deviations), in the same direction, for anethole triplet vs. anethole-d_2 triplet. Rigorous statistical analysis[16] shows that this (admittedly modest) effect is significant at the 99% confidence level. Our isotope effect thus reinforces the conclusion from the analogous stilbene one[15] that there is at least some contribution from vinyl C–H bonds in inducing the decay of these twisted triplets. Our alkylation effect is nicely convergent with the isotope effects, in that replacement of H by alkyl should increase the lifetime analogously to the replacement of H by D. Both decrease the number of vinyl C–H bonds, the motions of which contribute to the decay.

An alternate explanation could be that alkylation alters the electronic structure of the triplet, which in turn affects the lifetime. Note that the effect of *p*-methoxy in **2** vs. **9** apparently requires such a contribution. Alkylation, through hyperconjugative delocalization, could increase the average distance between the unpaired electrons, thus[14] decreasing spin–orbit coupling and increasing the lifetime. However, on the basis of alkyl radical models, EPR spectra of which show that hyperconjugation is rather modest,[17] we expect such an effect to be small. It is in any case difficult to see how this mechanism per se could predict the observed isotope effects. We conclude that variation of electronic structure with alkyl substitution is at best an incomplete explanation.

The involvement of nuclear motions in decay of triplet biradicaloids follows the suggestion of Shaik and Epiotis[18] that such effects should be important. Further confirmation of this conclusion could have profound consequences for the mechanisms and dynamics of triplet-state photoreactions.

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(16) G. W. Snedecor and W. G. Cochran, "Statistical Methods", 6th ed., Iowa State University Press, Ames, IA, 1967, pp 114–116.

(17) See M. Symons, "Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy", Wiley, New York, 1968, p 41 ff.

(18) (a) S. Shaik and N. D. Epiotis, *J. Am. Chem. Soc.*, **100**, 18 (1978); (b) S. Shaik, *ibid.*, **101**, 2736, 3184 (1979).

Fast Oxidants for NADH and Electrochemical Discrimination between Ascorbic Acid and NADH

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The ubiquity of NADH and ascorbate makes their oxidation chemistry of special significance. We report here on chemically catalyzed, electrochemical oxidations. The study has demonstrated that the oxidized forms of aromatic diamines, which are flavin analogues, are very active NADH and ascorbate oxidants and revealed a crucial aspect of the NADH oxidation mechanism. This mechanistic knowledge led to the discovery of a catalyst which gave separate electrochemical responses for NADH and ascorbate. A unique method for the quantitative analysis of either compound using differential pulse voltammetry was then demonstrated.

NADH is electrochemically oxidized[1] in a process which has a large activation energy (overpotential). The electrochemical response is difficult to reproduce and highly dependent on the nature of the electrode surface and its history. As shown by Kuwana and co-workers,[2] this slow oxidation at the electrode can be catalyzed by certain other redox couples in the solution. *o*-Hydroquinones are, for example, electrochemically oxidized with a low activation energy and the resulting *o*-quinones will in turn rapidly oxidize NADH in the solution near the electrode. This approach has been further developed by binding a hydroquinone to an electrode surface and using the resulting electrode to oxidize NADH by an analogous two-stage process.[2,3]

We have studied several diamine redox couples in solution as catalysts. These were chosen for study because they are readily available and the oxidized forms are related in structure to oxidized flavins and natural quinones which are known to be NADH oxidants.[4] Consider first the electrochemical behavior of 1,4-diaminobenzene (**1a**). Cyclic voltammograms were measured in pH 7.0 aqueous solution (phosphate buffer) on a polished vitreous carbon disk electrode of area 7.07 mm^2. An SCE reference was employed. A voltammogram showing the quasi-reversible couple (ΔE_p = 40 mV at ν = 50 mV s^{-1}) for oxidation of **1a** is shown in Figure 1a. This voltammogram is exactly what one expects from many previous studies on this redox system.[5] At 0.20 V, **1a** produces a quinone diimine **2a**, which is stable on this time scale.[6]

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(2) (a) Tse, D. C.-S.; Kuwana, T. *Anal. Chem.* **1978**, *50*, 1315. (b) Electroanalytical schemes involving NADH, NAD$^+$, enzymes, and redox reagents have also been discussed. See references in: Cheng, F. S.; Christian, G. D. *Ibid.* **1977**, *49*, 1785.

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(5) See references in: Adams, R. N. "Electrochemistry at Solid Electrodes"; Marcel Dekker: New York, 1969.

(6) The pK_a of **1a** is 6.2. The pK_a of **2a** is unknown.

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